

## Corrosion Behavior of Ti-6Al-7Nb Alloy in Biological Solution for Dentistry Applications

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The corrosion behavior of titanium alloy without vanadium Ti-6Al-7Nb under simulated biological conditions was investigated and compared with that of titanium and Ti-6Al-4V alloy, which employed as biomaterials. The aim of the present study was to evaluate their corrosion performance through the analysis of open circuit potential (OCP) and corrosion resistance using electrochemical impedance spectroscopy (EIS) tests. A high corrosion resistance was obtained for Ti-6Al-7Nb compared to that of titanium and Ti-6Al-4V alloy, indicating a typical passive behavior for Ti-6Al-7Nb alloy, which can be attributed to a highly stable film formed on Ti-6Al-7Nb alloy in Hank's solution. The corrosion resistance of the three electrodes was in the order of Ti > Ti-6Al-7Nb > Ti-6Al-4V. Thus, Ti-6Al-7Nb can be used instead of Ti-6Al-4V to avoid the problems related with vanadium.

**Keywords:** Ti-6Al-7Nb, Ti-6Al-4V, Titanium alloys, Dentistry applications, EIS, Hank's solution

### 1. INTRODUCTION

Titanium alloys are used in a large number of applications ranging from aerospace to marine to chemical industries because of their excellent corrosion resistance. Such a high and remarkable corrosion resistance is attributed to a very stable oxide film formed on the alloy surface [1]. Metallic materials are being increasingly used in medical applications as implants to restore lost functions or replace organs functioning below acceptable levels. Titanium alloys are among the most used metallic biomaterials, particularly for orthopedic applications [2]. They possess a set of suitable properties for these applications such as low specific weight, excellent mechanical properties, good resistance to corrosion in biological fluids and very low toxicity for the organism [3].

The demand for metallic materials in medical and dental devices continuously increases being very important in the medical field mainly due to their mechanical properties. However, the corrosion of the metallic implants is critical because it could affect negatively the biocompatibility and the mechanical integrity. Large concentration of metallic cations coming from the prosthesis can result in biologically adverse reactions and might lead to mechanical failure of the implant [4]. In recent years, biocompatible alloys have been intensively studied with a strong emphasis on their corrosion behavior, surface properties, and biocompatibility in implants [5]. Titanium and its alloys are widely used as implant materials for failed hard tissue because of excellent corrosion resistance and good compatibility with bone [6-9]. This high degree of biocompatibility is attributed to the natural formation of a protective, stable oxide layer on the surface [9,10].

The Ti-6Al-4V alloy with ( $\alpha+\beta$ ) structure was the first titanium alloy registered as implant material in the ASTM standards (F-136-84) [11]. There has been considerable interest especially in the use of the alloy Ti-6Al-4V for orthopedic implants because of its fatigue strength and biocompatibility. However, this alloy has certain limitations. Metal ions are released from the Ti-6Al-4V implant to the bloodstream and these may cause local irritation of the tissues surrounding the implant [6]. Studies have indicated that vanadium, used to stabilize the  $\beta$ -phase, produces oxides harmful to the human body. The toxicity of vanadium has pushed forward the search for materials to replace Ti-6Al-4V [12]. Thus, many titanium-based alloys with different alloying elements were developed as implants materials, with mechanical properties comparable to the Ti-6Al-4V, and safe for human use. The modified Ti alloys containing Nb, Zr, Ta, Sn, Pd with various percentages [13]. An example of them, Ti-6Al-7Nb was developed [12].

One determining factor for the success of new alloys as biomaterials is their corrosion behavior. Therefore, the in vitro evaluation of their corrosion parameters is one of the first steps in the development of new biomaterials. Additionally, the corrosion behavior of a material strongly depends on the presence of a protective passive film, i.e. is mainly a surface phenomenon. Consequently, the determination of the passive film composition complements the in vitro corrosion evaluation. The characterization of the surface composition is of high interest also because most external layers of a biomaterial will be in direct contact with biological tissues [13].

In the present work, the corrosion behavior of Ti-6Al-7Nb alloy was studied, and then compared with titanium and Ti-6Al-4V alloy. The electrochemical methods, like open-circuit potential measurements and electrochemical impedance spectroscopy, were carried out in order to study the corrosion behavior of metals.

## 2. EXPERIMENTAL PROCEDURES

The electrochemical study was used to compare the three materials: Ti, Ti-6Al-7Nb, and Ti-6Al-4V. The composition of Ti alloys as received used in this investigation is given in Table 1. The electrodes were prepared by epoxy cold resin mounting of alloys, leaving areas for exposure to the electrolyte of 0.19, 0.20, and 0.28 cm<sup>2</sup> for the Ti, Ti-6Al-7Nb, and Ti-6Al-4V, respectively. All the samples surfaces were abraded to 2500 grid using Phoenix 4000 (Buehler, Germany) then polished

with alumina paste. They washed with double distilled water followed by ultrasonic cleaning with ethanol for 10 minutes.

The measurements were performed in conventional three-electrode cell. The counter electrode was a Pt plate, and all potentials were measured against a saturated calomel electrode (SCE) connected to the cell via a Luggin probe.

**Table 1.** The composition of studied electrodes

Alloys	Abbreviations	Elements (%)			
		Al	Nb	V	Ti
Ti	T	-	-	-	-
Ti-6Al-7Nb	TAN	6	7	-	Balance
Ti-6Al-4V	TAV	6	-	4	Balance

In order to simulate the physiological conditions of human body, Hank's solution was used for *in vitro* corrosion studies and its chemical composition is given in Table 2 [14-19]. It is prepared with double distilled water and analytical grade reagents.

**Table 2.** The composition of Hank's solution [11-15].

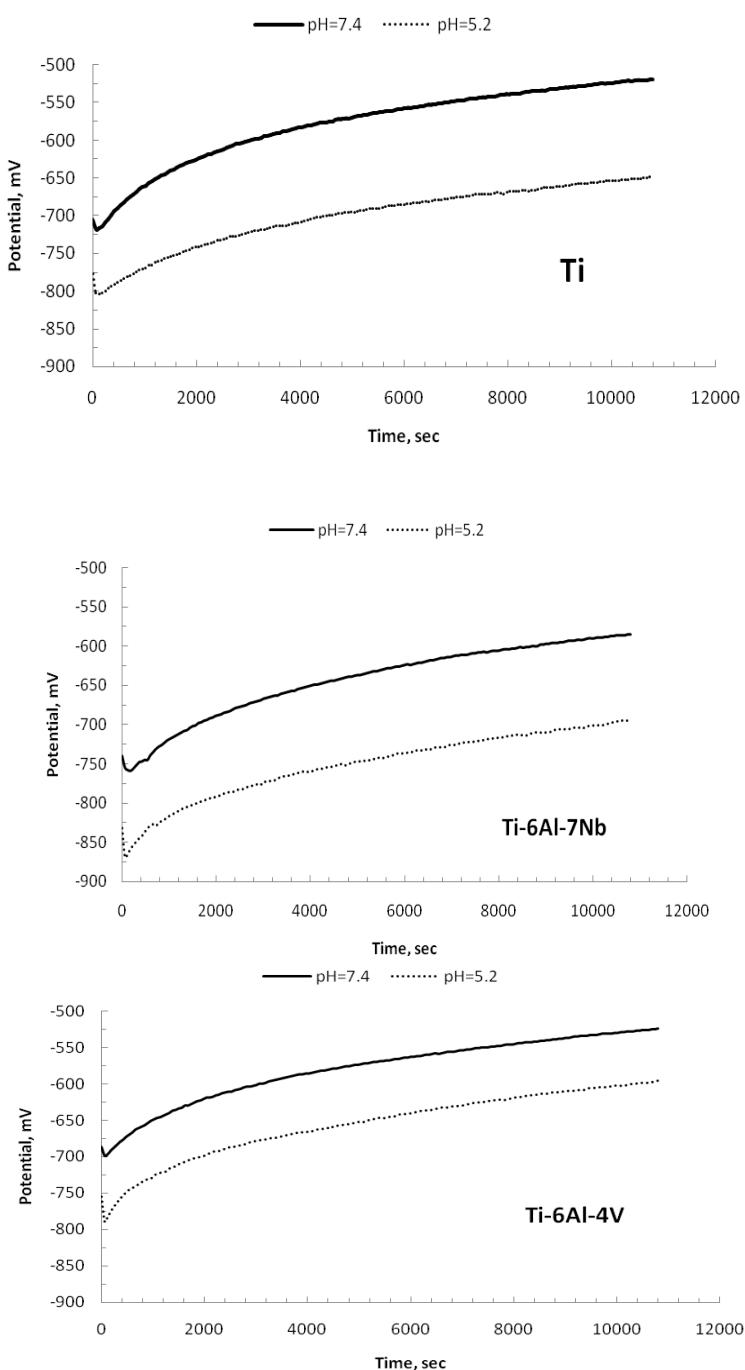
Reagent	Composition g\l
NaCl	8.00
KCl	0.40
NaHCO <sub>3</sub>	0.35
CaCl <sub>2</sub>	0.14
MgCl <sub>2</sub> .6H <sub>2</sub> O	0.10
Na <sub>2</sub> HPO <sub>4</sub> .2H <sub>2</sub> O	0.06
KH <sub>2</sub> PO <sub>4</sub>	0.06
MgSO <sub>4</sub> .7H <sub>2</sub> O	0.06
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1.00

The electrodes were immersed in Hank's solution at pH of 7.40, 5.20 (since the pH of the hard tissue into which a material is implanted decrease to approximately 5.2 and then recovers to 7.40 within two weeks[20]), and thermostatically controlled at temperature of 37°C . Fresh solution was used for each experiment. The experiments were repeated several times to ensure reproducibility of the electrochemical curves. In the experiment, the evolution of the open circuit potential; i.e. corrosion potential, as a function of immersion time was measured for three hours, then electrochemical impedance spectroscopy was recorded. These measurements were done by using the electrochemical workstation Zahner IM6e (Zahner Elektrik, GmbH, Kronach, Germany).

### 3. RESULTS AND DISCUSSION

#### 3.1. Open-circuit potential (OCP) measurements

The chemical properties of the oxide layer play an important role in the biocompatibility of titanium implants and the surrounding tissues and it must not break down if the implant is to be successful [21]. From the medical point of view, the biocompatibility of a prosthetic implant is determined by the stability of the oxide film and the ability to incorporate ions from solution [22]. Thus, determination of the chemical interaction of metallic materials/bone prosthesis with the body fluid environment is essential in order to understand their stability in the human body.



**Figure 1.** The OCPs of T, TAN, and TAV in aerated Hank's solution at two pH [7.40 and 5.20] at 37°C measured for three hours

One simple way to study the corrosion behavior, i.e. film formation and passivation of implants/alloys in a solution, is to monitor the open-circuit electrode potential (OCP) as a function of time. Increasing the potential in the positive direction indicates the formation of a passive film, and a steady state potential indicates that the film remains intact and protective. A drop of potential in the negative direction indicates breaks in the film, dissolution of the film, or no film formation [13].

The OCPs of T, TAN, and TAV in Hank's solution at two pH [7.40 and 5.20] measured for three hours are shown in Fig.1 . The results were fairly reproducible, and it can be clearly seen that all the curves are quite similar and run nearly parallel to each other in all conditions. It is observed that there is an initial shift of potential in the active direction within the initial few minutes followed by a continuous rise in potential towards noble direction to attain finally the steady state potentials. These results revealed a presence of competition between film dissolution and film formation, which end by a potential indicating thickness and self healing of surface film. The potential variation rate, which reflects oxide formation rate, was high after few minutes of immersion, and decreased with time to reach a steady state.

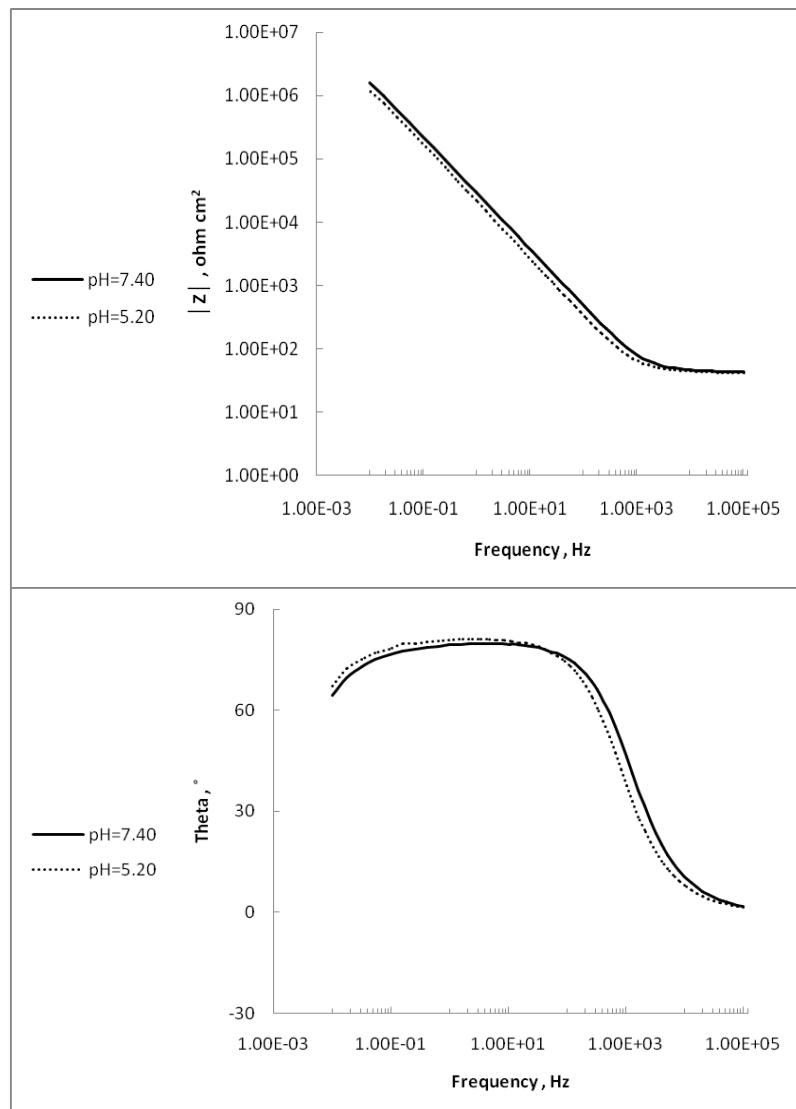
In pH 5.20, the OCP is more negative compared with that of pH 7.40, which means that the formed film is stable in neutral medium than in acidic one. Hodgson et al. [19] reported on the time evolution of some properties of passive films on Ti, Ti-6Al-4V, and Ti-6AL-7Nb in solutions simulating physiological conditions. Of particular interest were the selective interactions of phosphate and calcium ions present in the simulated body fluid with oxide films, immediately after exposure to the electrolyte interface could be detected already within the first hour of exposure at 37°C and were found to be the ions present in simulated body fluid to interact with titanium oxide surface, which is responsible for both their corrosion resistance and their biocompatibility.

The steady state potential, which indicates corrosion potential ( $E_{corr}$ ), is much more positive for  $T > TAN > TAV$ . Ti showed nobler potential than the alloys, as seen by Raman et al [17], which can be attributed to the formation of a pure  $TiO_2$  passive film, compared to the mixed oxide formation on the alloys. However, the enhanced passive film formation for the alloy Ti-6Al-7Nb can be attributed to the presence of Nb. Also, the Nb cations improve the passivation properties of surface film by decreasing the concentration of anion vacancies present on titanium oxide film. These anion vacancies are generated by the presence of lower titanium oxidation states [20]. The better corrosion performance of Ti-6Al-7Nb alloys in Hank's solution has also been reported earlier by the same authors [23,24].

### *3.2. Electrochemical impedance spectroscopy measurements :*

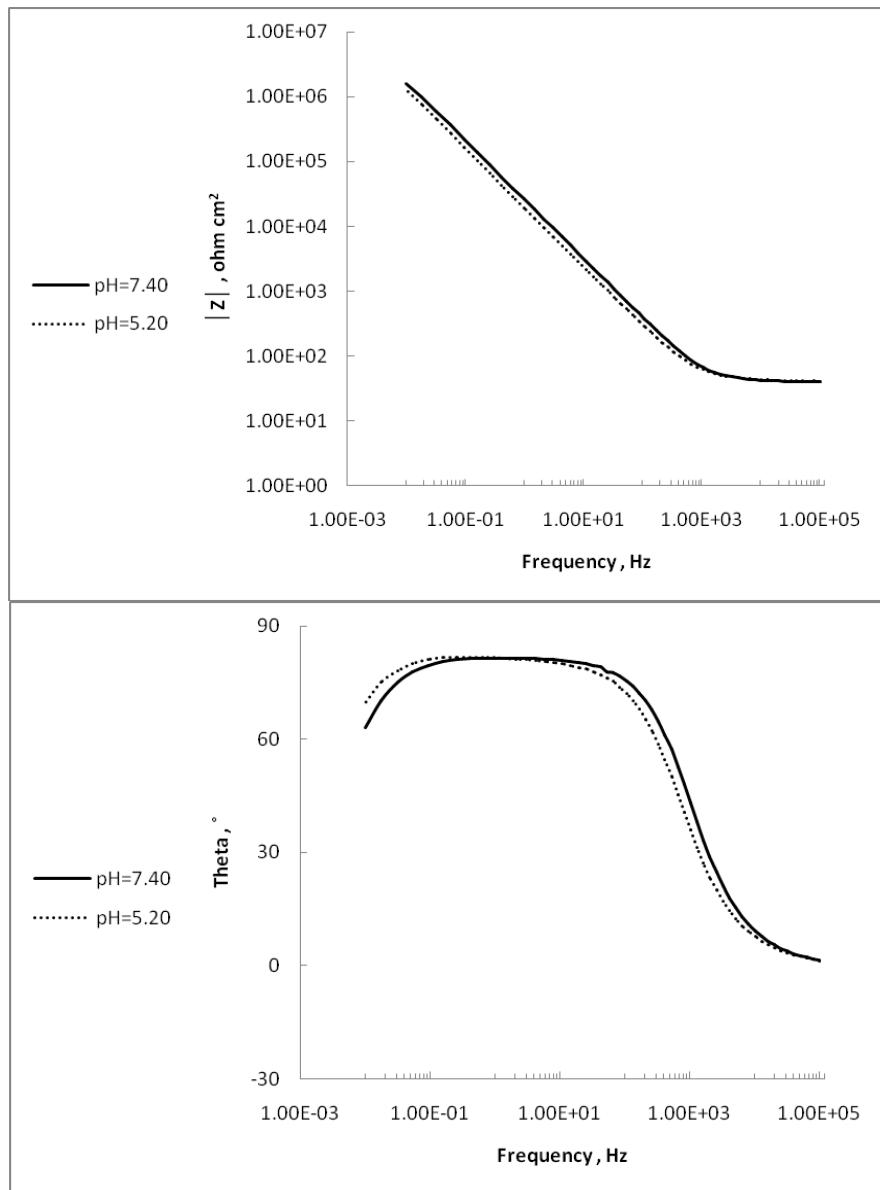
Impedance measurements are one of the most useful and informative methods of corrosion assessment [14–18]. The response of a corroding specimen to an applied small amplitude signal will depend on the frequency of the signal. The magnitude and phase shift at each frequency is noted, and the corrosion cell response is expressed as a combination of resistive, capacitive, and inductive components. The impedance behavior of a specimen can be expressed either in Bode plots of impedance modulus ( $|Z|$ ) as a function of frequency or in Nyquist plots of  $Z''(\omega)$  as a function of  $Z'(\omega)$ , where  $\omega=2\pi f$  [13].

The results of the impedance measurements for pure Ti and its alloys in Hank's solution are presented as Bode plots in Figures 2-4. The spectra show that in the higher frequency region,  $\log |Z|$  tends to become constant, with the phase angle values falling rapidly towards zero with increasing frequency.



**Figure 2.** Impedance plots of T in aerated Hank's solution at two pH [7.40 and 5.20] and 37°C after three hours

This is a response typical of the resistive behavior and corresponds to the solution resistance. Inside the medium and low frequency regions, the systems behave differently.



**Figure 3.** Impedance plots of TAN in aerated Hank's solution at two pH [7.40 and 5.20] and 37°C after three hours.

A highly capacitive behavior, typical of passive materials, is indicated from medium to low frequencies by phase angles approaching 90°, suggesting that a highly stable film is formed on tested alloy in the electrolyte used.

The large phase angle peak could be indicative of the interaction of at least two time constants. In the same frequency range, a linear relationship between  $\log |Z|$  and  $\log f$  is observed for all samples with slopes approach one.

According to literature [25-27] the film on Ti alloys is composed of a bi-layered oxide consisting of a porous outer layer and a barrier inner layer. In work performed by Lavos-Valereto et al.[27] and by Pan et al. [28] for titanium immersed in saline solution, the model assumes that the oxide layer on the Ti alloys consists of a barrier-like inner layer and a porous outer layer. In this

model, Fig. 5,  $R_s$  corresponds to the resistance of the solution,  $R_p$  to the resistance of the porous layer,  $R_b$  to the resistance of the barrier layer,  $C_p$  to the capacitance of the porous layer and  $C_b$  to the capacitance of the barrier layer.

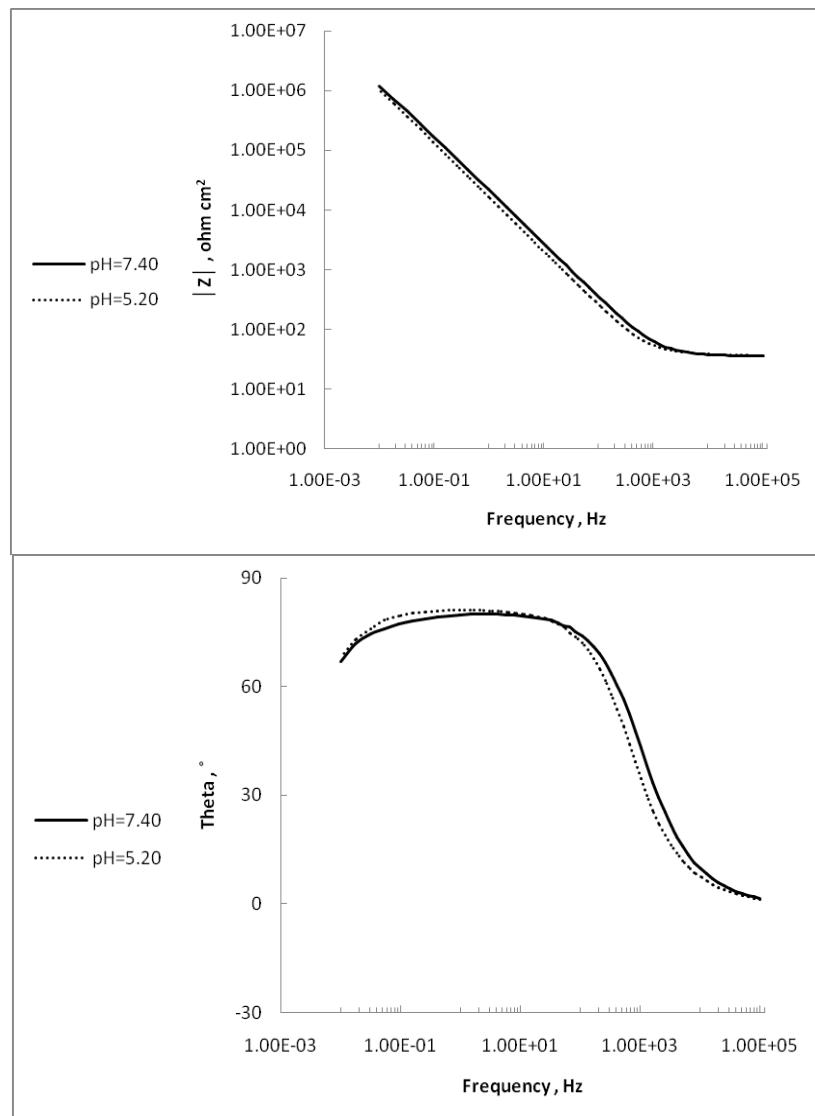
A constant-phase element representing a shift from the ideal capacitor was used instead of the capacitance itself, for simplicity. The impedance of a phase element is defined as  $Z_{CPE} = [C(j\omega)^\alpha]^{-1}$ , where  $-1 \leq \alpha \leq 1$ . The value of  $\alpha$  is associated with the non-uniform distribution of current as a result of roughness and surface defects.

The resistance and capacitance values of the porous and barrier layers are given in Table 3. High impedance values were obtained from medium to low frequencies for the Ti alloy suggesting high corrosion resistance in the electrolyte used. This result supports the passive behavior of the alloy, indicated by the open circuit potential measurements. According to the proposed model, the inner barrier layer, whose resistance values,  $R_b$ , are significantly larger than the values associated to the outer porous layer,  $R_p$  as shown in Table 3.

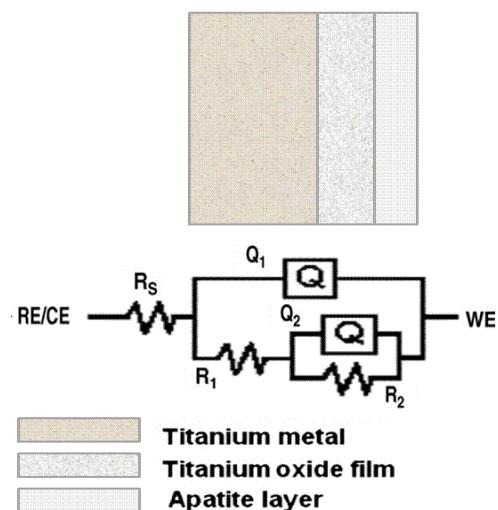
**Table 3.** Values of fitting parameters for T, TAN, and TAV after immersion in Hank's solution of two different pH's for 3 hours at 37°C.

Electrode	pH	$\Omega \text{ cm}^2$		$\mu\text{F cm}^{-2}$	$\text{K}\Omega$		$\mu\text{F cm}^{-2}$	$\text{M}\Omega$	
		$R_s$	$Q_1$		$n_1$	$R_1$ $\text{cm}^2$		$n_2$	$R_2$ $\text{cm}^{-2}$
T	7.40	42.96	2.15		0.96	77.94	1.65	0.85	9.06
	5.20	41.86	3.94		0.97	61.40	3.10	0.86	6.30
TAN	7.40	40.04	5.19		0.91	62.22	2.00	0.91	7.86
	5.20	41.12	6.67		0.91	55.30	4.12	0.91	5.78
TAV	7.40	38.52	11.35		0.78	43.53	10.93	0.85	6.91
	5.20	40.23	13.71		0.71	38.11	11.16	0.91	5.53

These results indicate that the protection provided by the passive layer is predominantly due to the barrier layer. It has been previously proposed that while the corrosion resistance of the Ti alloy is ascribed to the barrier layer, the ability to osseointegrate should be attributed to the presence of the porous layer [27]. The porous oxide may become hydrated and ions forming Hank's solution may be easily incorporated into the pores and further precipitate leading to corrosion or self-healing. On the other hand, it can be seen that the resistance of TAN is higher than that of TAV, as indicative from open circuit potential. The corrosion resistance of the three electrodes was in the order of T > TAN > TAV.

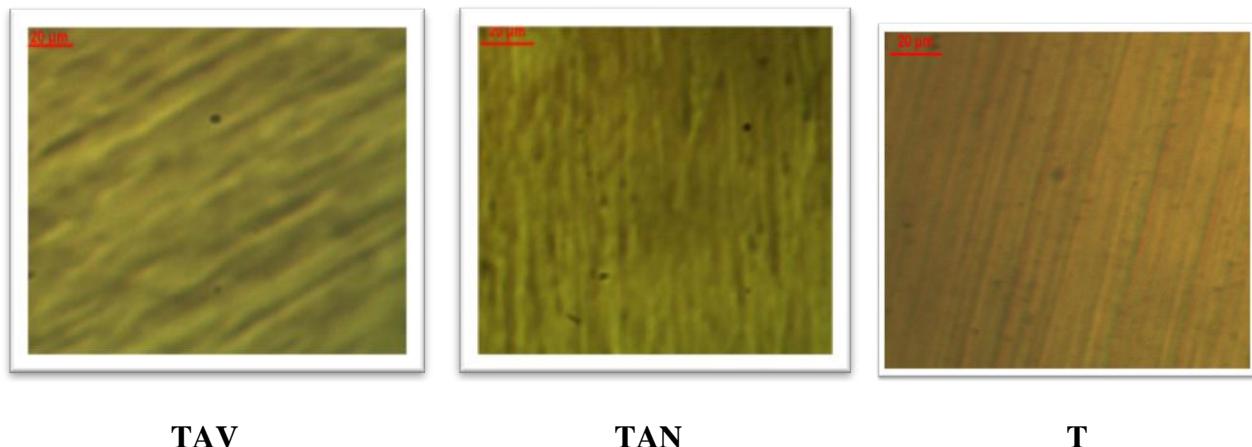


**Figure 4.** Impedance plots of TAV in aerated Hank's solution at two pH [7.40 and 5.20] and 37°C after three hours.

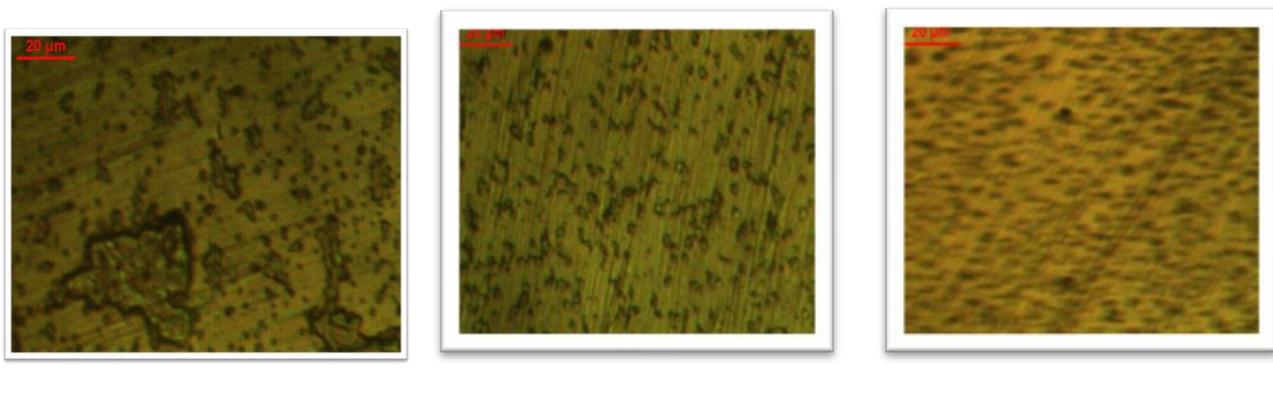


**Figure 5.** Equivalent electrical circuit used to fit the impedance spectra of T, TAN, and TAV in aerated Hank's solution at two pH [7.40 and 5.20] and 37°C.

All these results were confirmed by optical micrographs as shown in Figs. 6, 7 & 8. It was seen that the image for all samples before immersion is smooth as shown in Fig. 6, however after immersion in Hank's solution at pH = 5.2 at 37°C, the order is as follows T > TAN > TAV, where TAV alloy is much corroded as shown in Fig. 7. After increasing pH to 7.4 (neutral), the corrosion for the three electrodes decrease as shown in Fig. 8 with the same order as before. This means that TAN alloy can be mostly used due to lower cost than T and have high passivity near that of T and higher than TAV. Thus, it can be used especially at pH = 7.4 in human body. The results may be caused by the different distribution of alloying elements in microscopic scale and the microstructure of alloys, which are the fundamental reasons for the metal corrosion morphology and corrosion resistance.

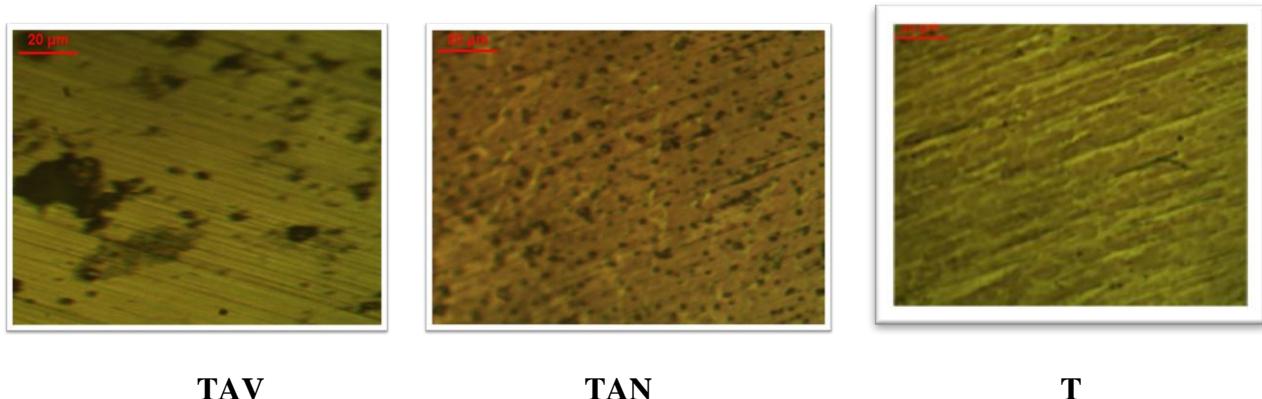


**Figure 6.** Optical micrographs before immersion



**Figure 7.** Optical micrographs after three hours of in Hank's solution at pH=5.2 and 37°C.

The enhanced passive film formation for the alloy Ti–6Al– 7Nb can be attributed to the presence of Nb. The effects of Nb as an alloying element in stabilizing the surface films on Ti based alloys have been reported [29].



**Figure 8.** Optical micrographs after three hours of in Hank's solution at pH=7.4 and 37°C.

Also, the Nb cations improve the passivation properties of surface film by decreasing the concentration of anion vacancies present on titanium oxide film. These anion vacancies are generated by the presence of lower titanium oxidation states. Hence, the low current density obtained for Ti-6Al-7Nb compared to Ti-6Al-4V might be due to the effect of Nb in the passive film of the former. The better corrosion performance of Ti-6Al-7Nb alloys in Hanks solution has also been reported earlier by the same authors [20,29].

#### 4. CONCLUSIONS

The electrochemical techniques used in this investigation led to the following conclusions. Very low corrosion rates were obtained for Ti6Al7Nb, like to those for titanium and Ti6Al4V alloy in Hank's solution. The impedance results indicated that the film formed on the Ti and its alloys is composed of a bi-layered oxide consisting of an inner barrier layer associated with high impedance and responsible for the corrosion of the sample, and an outer porous layer, of lower impedance, which apparently facilitates the osseointegration.

The results revealed that Ti and its alloys have high corrosion resistance. The corrosion resistance of the three electrodes was in the order of T > TAN > TAV. Thus, Ti-6Al-7Nb can be used instead of Ti-6Al-4V to avoid the problems related with vanadium.

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